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An Investigation of II-VI Superlattice
Deposition by Laser Photochemical Techniques

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Richard J. Stirn
Akbar Nouhi
Gouri Radhakrishnan

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The objectives of this research program are to develop metalorganic chemical vapor deposition (MOCVD) techniques for Mn-bearing II-VI ternary compounds epitaxially grown on GaAs substrates, and to explore the usefulness of UV laser assist for deposition of super-lattice structures of wider bandgap II-VI binary compounds. For the first time, high quality single-crystal (111) $Cd_{1-x}Mn_xTe$ was grown by conventional MOCVD on (100) GaAs wafers with $0 \leq x \leq 0.6$. High resolution cross-sectional transmission electron microscopy was used for structural characterization, showing atomically abrupt interfaces, but different microstructures within the epi-film depending on growth temperature. UV absorption spectra of a number of metalalkyl sources for Cd, Zn, Se, and Te were measured and optical absorption cross sections calculated. Preliminary depositions of CdTe and ZnTe films on glass substrates were made at 200°C with UV excitation provided by an excimer gas laser operating at 193 nm and by using a parallel beam geometry. Some optical and X-ray diffraction data are presented as well as a description of the low pressure laser photochemical deposition system. Keywords: Cadmium Telluride, Zinc Telluride.

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ABSTRACT

The objectives of this research program are to develop metalorganic chemical vapor deposition (MOCVD) techniques for Mn-bearing II-VI ternary compounds epitaxially grown on GaAs substrates, and to explore the usefulness of UV laser assist for deposition of superlattice structures of wider bandgap II-VI binary compounds. For the first time, high quality single-crystal (111) $Cd_{1-x}Mn_xTe$ was grown by conventional MOCVD on (100) GaAs wafers with $0 \leq x \leq 0.6$. High resolution cross-sectional transmission electron microscopy was used for structural characterization, showing atomically abrupt interfaces, but different microstructures within the epi-film depending on growth temperature. Minimum growth temperatures are about 410°C, the limitation determined by the thermal cracking of the Mn source (tricarbonyl methyl cyclopentadienyl manganese).

UV abosrpcion spectra of a number of metalalkyl sources for Cd, Zn, Se, and Te were measured and optical absorption cross sections calculated. Preliminary depositions of CdTe and ZnTe films on glass substrates were made at 200°C with UV excitation provided by an excimer gas laser operating at 193 nm and by using a parallel beam geometry. Some optical and X-ray diffraction data are presented as well as a description of the low pressure laser photochemical deposition system.

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I.   INTRODUCTION

A.   LASER PHOTOCHEMICAL DEPOSITION

The use of ultraviolet (UV) and visible wavelength photon-assisted semiconductor processing techniques is rapidly expanding as an area of device and materials research. Such techniques, particularly involving laser sources, include: 1) direct writing of metals, silicides, or polysilicon for VLSI interconnections, 2) etching of semiconductors, metals and dielectrics, 3) deposition of thin films locally by low-temperature photochemical or thermally-activated reactions, and 4) doping of compound and elemental semiconductors, including submicrometer line widths.

In general, photochemical processing is seen to be advantageous because of: 1) lower temperatures possible, 2) absence of ionizing radiation, 3) broad area as well as selective small area geometries, and 4) selective reactive processing because of wavelength control and optical tranparency of external gases or liquids. A number of review articles have been written giving examples of research results and their respective references (Refs. 1-4).

Excimer lasers in particular are playing a vital role in the laser processing of semiconductors. Excimer lasers provide photon energies in the ultraviolet that range from 6.4 eV (ArF) to 3.5 eV (XeF), energies sufficient for the breaking of chemical bonds initiated by photon absorption. In addition to initiating photochemical processes, the excimer lasers can also induce thermally-driven reactions as a result of instant local heating provided by a very short pulse (10-20 ns). A very important advantage that laser-induced deposition offers is that of low-temperature growth. It has been demonstrated by several groups that laser-initiated deposition of semiconductors occurs typically at temperatures 200-300°C lower than required for conventional chemical vapor deposition (Refs. 5-9).

These studies have raised interesting questions concerning differences in film quality, or even whether growth will occur, depending on whether the laser beam is parallel to and just above the substrate, or whether the beam is

incident on the substrate surface, as well as the beam pulse energy used. Even in the case where gas dissociation occurs in a reaction volume near the substrate when using a parallel beam, enhanced growth rates and film quality are obtained when a considerably lower UV fluence than that used in the parallel beam irradiates the surface. There have been reports that film growth is initiated at substrate temperatures well below those normally required for conventional CVD only when the surface is irradiated (Ref. 10, for example). Additionally, surface irradiation seems to markedly reduce the measured carbon content in the deposited films.

The role of UV photons incident to the surface may be to: 1) catalyze or activate surface bonding states which then provide nucleation sites, 2) convert physisorbed adatoms to chemically – bonded adatoms, or 3) activate or enhance adatom diffusion on the surface, leading possibly to improved film quality and stoichiometry. Certainly, any experimental study of laser photochemical deposition (LPD) for new materials should closely investigate such phenomena. For example, it may be possible to distinguish between photochemical and thermal effects by changing the wavelength of the perpendicular radiation.

The use of LPD for low-temperature deposition of compound semiconductors has only begun the last several years, primarily focused on GaAs and InP. Investigation of II-VI compound deposition by LPD to date is extremely limited with the exception of $Cd_xHg_{1-x}Te$ materials. The latter has been studied for several years in Great Britain (Refs. 11,12) and at AT&T Bell Laboratories (Ref. 13,14), for example, as an outgrowth of conventional MOCVD work. The reason for such interest is the infrared focal plane detector application and the need for low temperature deposition. Both groups are using conventional horizontal MOCVD reactor geometries and metal alkyl sources [diethyltellurium $(C_2H_5)_2Te$ and dimethylcadmium $(CH_3)_2Cd$] along with elemental Hg. Only the use of the UV output of Hg vapor arc lamps have been reported by these groups. There is disagreement between the two groups as to whether an inert gas, such as He, needs to be used in place of H_2 as a carrier gas in order to suppress gas phase reactions which prevent good epitaxial growth. Growth temperatures, in any case, were shown to be lowered by about 200°C (to 250°C) with the use of UV irradiation. An excimer laser source was successfully used for $Cd_xHg_{1-x}Te$ deposition, although no devices were reported (Ref. 8).

To our knowledge, ZnSe is the only other II-VI semiconductor which has been investigated for photo-assited CVD studies (Refs. 15,16). The first referenced work used only room temperature depositions and did not use a flowing gas system. Not surprisingly, the films were a nonstoichiometric mix of Zn and Se. The more recent Japanese work (Ref. 16) used flowing gases of diethylzinc $(C_2H_5)_2Zn$ and dimethylselenium $(CH_3)_2Se$, but again, only the relatively weak UV output of a low pressure Hg lamp was used. Interestingly, the alkyl sources were introduced into the growth chamber by the pressure difference and not with a carrier gas such as H_2 or He. Considerably different growth kinetics might be expected as a consequence. However, it was demonstrated that ZnSe films could be deposited with substrate temperatures as low as 150°C, whereas without the presence of the UV photons, growth ceased below about 350°C. Single crystal films were observed on GaAs substrates for substrate temperatures above 450°C. They also observed that irradiated films deposited on glass showed a high degree of (111) orientation for the polycrystalline films, while non-irradiated films had no preferential orientation.

B.   NOVEL II-VI STRUCTURES AND SUPERLATTICES

It was first pointed out by Esaki and Tsu in 1970 that novel electrical and optical effects might be obtained by imposing an artificial periodicity one or two orders of magnitude larger than the natural lattice spacing on a semiconductor crystal. Since then, considerable work has been done on what has become to be known as superlattice structures, but mostly on III-V class materials. GaAs/Ga(Al)As especially has been investigated because of their similar lattice constant.

However, several groups, including one at Sandia (Gordon Osbourn), have been demonstrating that the growth of superlattices with much more severely mismatched semiconductors can be accomplished. Alternating materials with considerably mismatched lattice constants can be grown with remarkable freedom from interface dislocations if the layers are sufficiently thin so that the misfit is elastically accommmodated. The first such system, originally looked at in the 1970's by Blakslee and Matthews at IBM, to be later developed at Sandia as a true strained layer superlattice (SLS) was Ga(As)P/GaP (Ref. 17).

Since then In(Ga)As/GaAs, InAs/GaSb, and Ga(As)Sb/GaAs have also been investigated--all grown by MBE.

Theoretical studies of SLS by Osbourn showed that the amount of strain offered another degree of freedom besides that of layer thickness and composition already demonstrated for matched superlattices. This permits one to independently vary the bandgap, lattice constant, optical properties and transport properties.

A particularly severe test of the freedom from interface defects of such SLS structures is their ability to sustain stimulated emission. Continuous room-temperature laser action has been demonstrated by several groups, initially by a University of Illinois group using Varian-grown SLS's of Ga(As)P/GaAs and Ga(In)As/GaAs (Ref. 18). However, these structures proved unstable after hours of operation under the high pumping power levels needed (about 10^3 watts/cm^2). Lower power applications, such as photodetectors and field-effect transistors, show no such metastability.

More recent theoretical studies (Refs. 19,20) of "band-gap or interface engineering" are showing ever more interesting new possibilities for applications to advanced microelectronic devices. Even more exciting is the fact that structures of SLS with appropriate buffer layers may also lead to advanced devices and sensors on silicon substrates, or to II-VI SLS structures on III-V compound opto-electronic device substrates.

The II-VI compounds are presently the latest material class (as well as amorphous materials) to be demonstrated as having potential for quantum well and superlattice structures with tunable properties. An even wider range of bandgaps are feasible with this class, ranging in equivalent wavelengths from the blue to the long infrared (IR) ($> 10 \mu m$).

The most studied system to date, again because of a very close lattice constant match and because of the high interest in monolithic IR focal plane detector arrays, is one comprising HgTe/CdTe multilayers. Thus, for example, with equal layer thicknesses of CdTe and HgTe, the cut-off wavelength can be

varied from about 2 to 30 μm by varying the layer thickness from 20 to 120 Å, respectively (Ref. 20).

Another very useful attribute of some superlattices for detector application, where one of the components has a high absorption coefficient as a result of a high density-of-states effective mass, is that the superlattice absorption coefficient can be significantly larger than that of the alloy with an identical bandgap. This is the case for HgTe/CdTe SL, for example, as compared to bulk HgCdTe. Thus, only 1 μm thickness may be sufficient for absorption of 10 μm radiation (Ref. 21). The work on this II-VI subset of materials is extensive and will not be reviewed here.

Development of a II-VI superlattice system with tunable bandgap energies in the visible is highly desirable. The additional possibility of incorporating magnetic ions by alloying a II-VI semiconductor with an appropriate binary chalcogenide would be of further interest for fundamental studies and novel device applications. Examples of the latter are $Cd_{1-x}Mn_xTe$, $Cd_{1-x}MnSe$, and $Hg_{1-x}Mn_xTe$. In the presence of an external magnetic field, interesting properties such as extraordinarily large Faraday rotation, giant negative magnetoresistance, and field-induced overlap of valence and conduction bands in the narrow bandgap materials are observed.

Two separate groups in this country have been quite active in growing (by MBE) and characterizing superlattices of II-VI materials other than HgTe/CdTe-teams at Purdue University and North Carolina State University. The most studied systems have been $Cd_{1-x}Mn_xTe/CdTe$ and $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$. These materials can be grown on GaAs substrates with a CdTe buffer layer.

Photoluminescence intensities were found to be three orders of magnitude greater than the intensity obtained from various bulk and thin film samples of $Cd_{1-x}Mn_xTe$ having uniform Mn concentrations (Ref. 22). It was later shown that both (111)- and (100)-oriented superlattices of $Cd_{1-x}Mn_xTe/CdTe$ on GaAs could be grown depending on the initial nucleation temperatures and the relative amount of residual oxide on the substrate (Ref. 23). Similar superlattices have been grown with these materials by MBE at North Carolina State on CdTe-buffered sapphire substrates (Ref. 24).

Stimulated laser emission (Ref. 25,26) and magnetically tunable (3.4 meV/T) quantum well laser structures (Ref. 27) in the Cd(Mn)Te family have been reported. Similarly, stimulated laser emission at 453 nm was reported in ZnSe/Zn(Mn)Se multiple quantum wells (Ref. 28). The later structure is interesting in that, whereas bulk $Zn_{1-x}Mn_xSe$ has a zincblende phase only for $x < 0.3$ (hexagonal phase above 0.3), only the zincblende phase (100) was observed over the entire range investigated $(0 < x < 0.51)$ for superlattice structures of $ZnSe/Zn_{1-x}Mn_xSe$ (Ref. 29).

One II-VI strained layer superlattice system under investigation by several groups in Japan is ZnSe/ZnTe because of its potential for tunable blue light-emitting diodes or lasers (Refs. 30-32). An interesting observation is that although there is a 7% lattice mismatch between the two binary components, each is only 3.5% mismatched to InP as a substrate, one being under expansion (ZnSe) and the other under compression (ZnTe). The work to date is too recent for device results to be reported; however, a change in peak photoluminesence position in energy from 2.01 to 1.81 eV was noted when the superlattice period was increased from 20 to 40 Å (Ref. 32). However, the absolute values of the energies were about 0.3 eV lower than calculated values (Ref. 29). More recently, the Tokyo Institute of Technology group reported the realization of both n- and p-type conduction in ZnSe/ZnTe SL by modulating the doping during growth by MBE (Ref. 33).

This research program has as its objective the development of a UV laser photochemical deposition system using metalorganic sources capable of depositing films of wider bandgap II-VI semiconductors, such as CdTe, ZnTe, or ZnSe, eventually as superlattice structures having very abrupt interfaces. Additionally, development of conventional metalorganic chemical vapor deposition (MOCVD) techniques for manganese-bearing II-VI ternary compounds epitaxially grown on GaAs substrates, and studies of the consequent interfacial epitaxial relationships using high resolution transmission electron microscopy have been undertaken.

II. FACILITIES

A. MOCVD OF Mn-BEARING II-VI TERNARIES

A conventional atmospheric pressure horizontal reactor tube growth system, originally built at Navtek Industries, was modified to accommodate Group II and VI metalalkyls, in particular that of the Mn source which requires heating. A further description of the system is given in Appendix A.

B. LASER PHOTOCHEMICAL DEPOSITION

Rather than adapting a conventional commercial MOCVD reactor system, a 10-in. diameter cylindrical stainless steel chamber with eight 2-3/4-in. Conflat flanges was used as shown in Figure 1. MgF_2 optics and windows were utilized to provide a normally incident UV laser beam geometry as shown, and by a collimating cylindrical telescope arrangement, an approximately 2-mm x 25-mm cross-section parallel beam geometry with about a 2-mm separation from the substrate. The latter passes into the chamber by a mirror through a window mounted in a flat top plate. All windows where UV light enters are purged with the buffer gas to prevent deposition on the window.

Vapors from the metalorganic sources carried by hydrogen gas are introduced to the reaction zone through an internal gas manifold connected to a run/vent switching manifold. Each source and buffer gas flow rate is controlled by a Unit 1200A Mass flow controller. Examples of the chemical sources are dimethyl-cadmium (DMCd), dimethylzinc (DMZn), dimethylselenium (DMSe), diethyltellurium (DETe), and di-isopropyltellurium (DIPT), all from Alfa Products, CVD Inc.

The system is pumped during a deposition run through the bottom plate (not shown in Fig. 1) by a chemical series Alcatel roughing pump, Model 2008A, and, for checking background pressures, by a 110 l/sec Pfeiffer turbomolecular pump. The chamber pressure is controlled by an adaptive controller/motorized throttle valve using a capacitance manometer for pressure sensing (Vacuum General, Inc.). A 700°C thermal cracker followed by a particulate filter is placed before the pumps to decompose unreacted gases. Considerable problems were
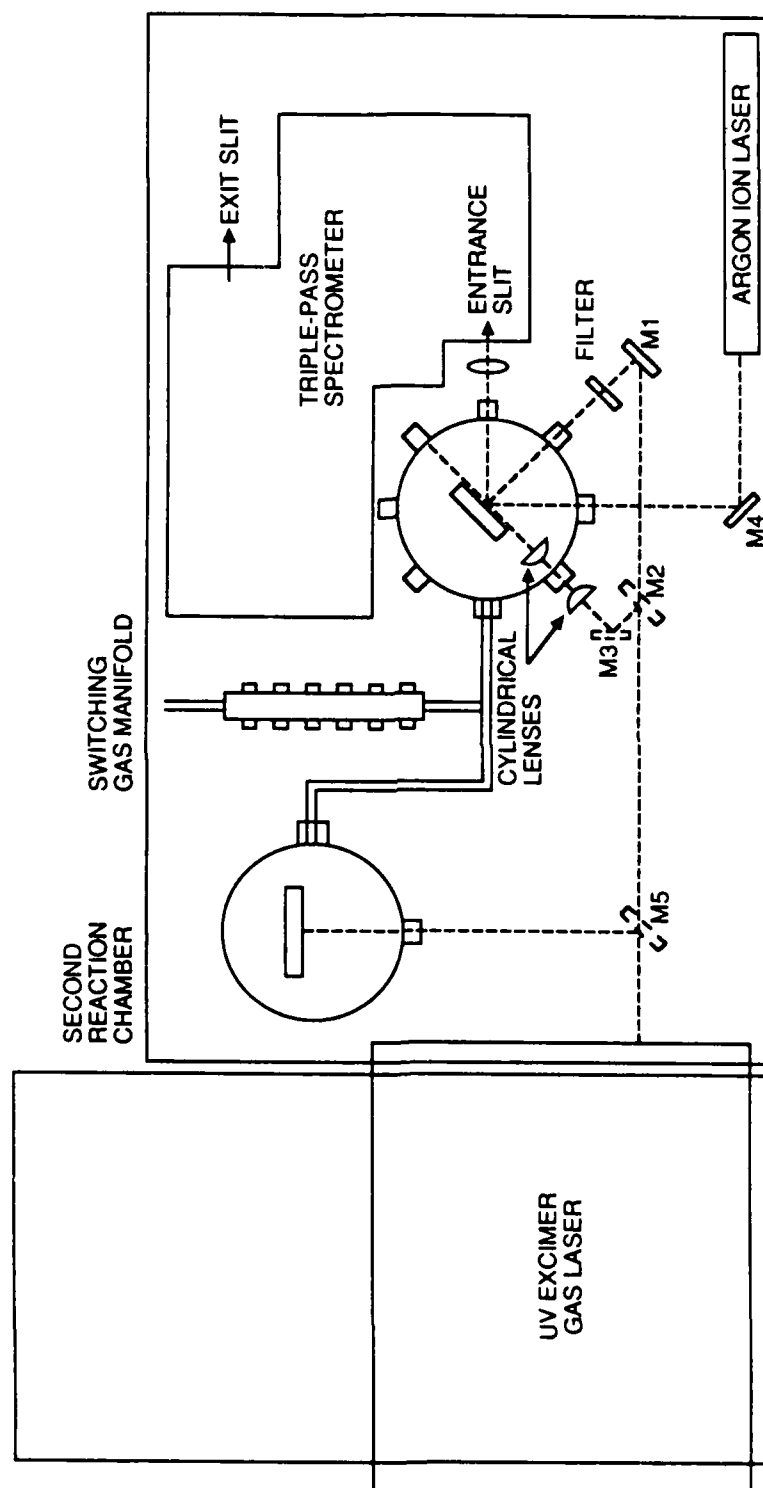
Figure 1. Physical layout of laser photochemical deposition facility. The spectrometer is planned for future research on in-situ, real-time optical characterization of the deposited films by laser Raman scattering.

initially encountered with pumps and pump oils before an adequate system was devised.

The source of UV radiation is an excimer gas laser (Questek Model 2000) operating at 193 nm (ArF) with up to 600 millijoules per pulse which, at a maximum repetition rate of 50 Hz, gives an average maximum power of 13 watts.

III. RESULTS AND DISCUSSION

A. MOCVD OF Mn-BEARING II-VI TERNARIES

As mentioned in the Introduction, a large amount of research has been reported on heteroepitaxial films of $Cd_{1-x}Mn_xTe$ including multilayer structures, where MBE has been the growth technique of preference. To our knowledge, there has been no report of (CdMn)Te deposition by MOCVD, although such studies have been reported for CdTe. The most likely reason is the lack of a reasonably high vapor pressure source for Mn.

We have for the first time successfully grown high quality single-crystal $Cd_{1-x}Mn_xTe$ with $0 \leq x < .60$ on GaAs substrates by MOCVD by utilizing specially heated sources, gas lines and valves, and reactor tube. A description of this work and some preliminary characterization of the material is given in a publication reproduced in Appendix A.

In collaboration with Prof. Jerome H. Mazur, Materials Science Department, University of Southern California, electron diffraction and high resolution transmission electron microscopy were used for analysis of the (CdMn)Te/GaAs interface. Preliminary studies were performed on samples from growth runs which did not intentionally modify the substrate precleaning nor initial growth conditions, either of which would be expected to influence the epitaxy relationships observed.

These early results were presented at the Fall Meeting of the Materials Research Society in Boston, Massachusetts, December, 1987. An extended abstract to be published in Vol. 102 of the proceedings is given in Appendix B.

B. LASER PHOTOCHEMICAL DEPOSITION

In order to effect a photochemical reaction, the absorption spectrum and molecular photochemistry of the candidate reactant molecules must be known. Most classical photochemistry has been carried out in solution and is not directly applicable to the gas phase reactions proposed. In general, however, small molecules are preferred because of their relatively high vapor pressure.

With their "simple" structure, organometallic molecules usually have their lowest energy electronic states in the UV or vacuum UV portion of the spectrum. Thus, just as with conventional metalorganic chemical vapor deposition, commercial metalalkyl liquid or solid sources will be utilized. Examples of these are given in Table I.

Table I. Physical properties of selected alkyls

Element	Compound	Melting Pt. °C	Boiling Pt. °C	Vapor Pressure Equation $\log_{10} P$ (mm Hg) $= B - A/T$ (°K)
Cd	dimethylcadmium	−4.5	105.5	$7.764 - 1850/T$
Zn	dimethylzinc	−42	46	$7.802 - 1560/T$
Mn	tricarbonyl(methyl-cyclopentadienyl)Mn	1.5	232	12 mm Hg @ 112°C
Mg	bis(cyclopentadienyl)Mg	176	---	$25.14 - 2.18 \ln T - 4198/T$
Te	diethyltelluride	---	138	$7.99 - 2093/T$
Te	di-isopropyltelluride	---	49	1.5 mm Hg @ 20°C
Se	diethylselenide	---	108	$7.905 - 1924/T$

UV spectra of the dimethylcadmium (DMCd) source, dimethylselenium (DMSe), and the two tellurium sources, diethyltelluride (DETe) and di-isopropyltelluride (DIPT), were measured with a Cary Model 17 spectrophotometer using 10-cm long quartz gas cells. Pressures of the sources were varied between 10 and 400 milli-Torr for purposes of calculating the optical absorption coefficients. The UV spectra are shown in Figure 2, with the calculated molar absorption coefficients and cross sections given in Table II. The data for DMCd and DETe agree well with results published by other groups (Refs. 34,35).

Using the parallel beam configuration, depositions of CdTe on glass sub-strates were made using DMCd and DIPT sources. We believe that this is the first attempt at using DIPT with photon-assist CVD of CdTe, as well as the first report of UV laser-assist deposition of CdTe using parallel laser beams. Previous studies used low- and high-pressure mercury arc lamps with the UV irradiation incident on the substrate surface (Refs. 11-14). The one report of the use of an excimer laser (Ref. 8) was also for normal incidence and involved HgCdTe films.

The initial experiments utilized direct pumping on the sources, which were held at room temperature, rather than bubbling a carrier gas of H_2 through

Table II. Molar absorption coefficients for the organometallic compounds calculated from UV absorption spectra

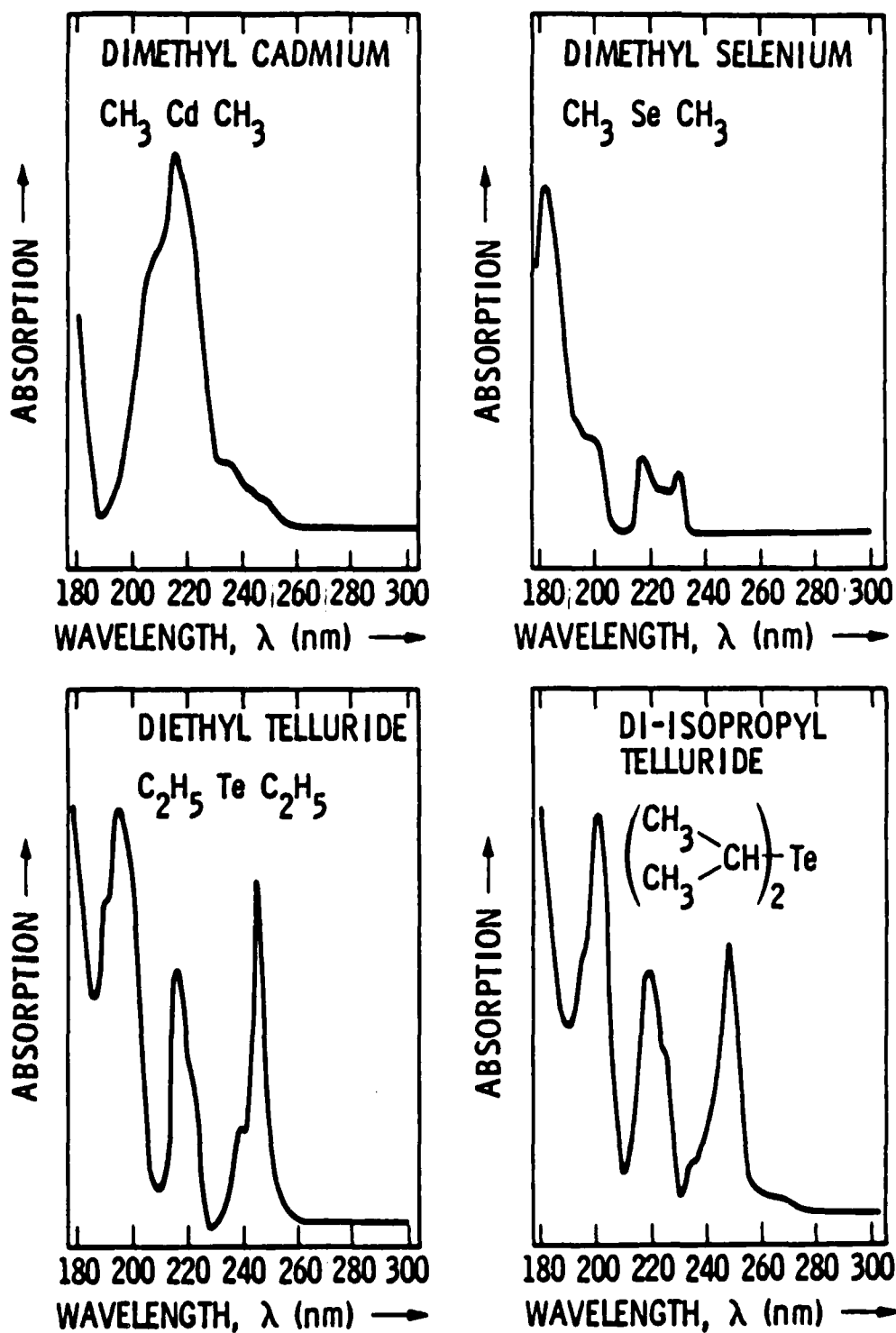| Compound	Molar Absorption Coefficients		Wavelength at
	$\epsilon(1\ mol^{-1}cm^{-1})$	$\sigma(molecule^{-1}cm^{-2})$	Peak Max, $\lambda(nm)$
dimethylcadmium	9370	3.59×10^{-17}	216
diethyltellurium	10398	3.58×10^{-17}	195
di-isopropyltellurium	10264	3.92×10^{-17}	200
dimethylselenium	473	1.92×10^{-17}	183

Figure 2. Ultraviolet absorption spectra of gaseous organometallic sources. The spectra were obtained at several pressures in the range of 10-400 mTorr.

them. The partial pressure of each was 200 mTorr with a total chamber pressure of 1 Torr including H_2 introduced for window purging. The substrate temperature was about 250°C as measured by a thermocouple. The excimer laser, operating at 193 nm with a repetition rate of 20 Hz, was power-locked at an energy of 50 mJoule per pulse as measured with a Gentec meter at the substrate location.

The optical transmission in the vicinity of the bandgap was measured (Fig. 3) with extrapolated transmission indicating a band edge of 1.51 eV, the known bandgap of CdTe. The film was very adherent and shiny, with a measured thickness in the central area indicating a deposition rate of 0.85 m/hr. The surface morphology was microscopically very smooth as shown by a scanning electron microscope (Fig. 4). An X-ray diffraction scan showed a preferred orientation of (111) for the polycrystalline film (Fig. 5), similar to that reported for ZnSe deposited by normally incident UV laser light (Ref. 16).

A few selected depositions were made of ZnTe and ZnSe in order to test out the sources involved, but a discussion of such films will need to be deferred to the next report when sufficient detail can be accumulated. It was noted that deposition rates appear to be noticeably lower for ZnSe than for either ZnTe or CdTe, perhaps due to the lower optical absorption at 193 nm for DMSe compared to DIPT (or DETe).

IV. FUTURE PLANS

The growth of CdMnTe on GaAs substrates by MOCVD will be continued with an objective of studying structure-property relationships and defect minimization at the interface. Success in growing high quality layers of the ternary should provide excellent lattice-matched buffer layers for subsequently grown HgCdTe layers for long wavelength infrared detectors.

An attempt will be made to induce purely (100) CdMnTe growth on off-axis (100) GaAs, investigating substrate orientation and surface precleaning, and MOCVD growth parameters, such as Te/Cd, Mn mole ratio, effect of surface passivation by pre-exposure to the Te source, and substrate temperature. Both
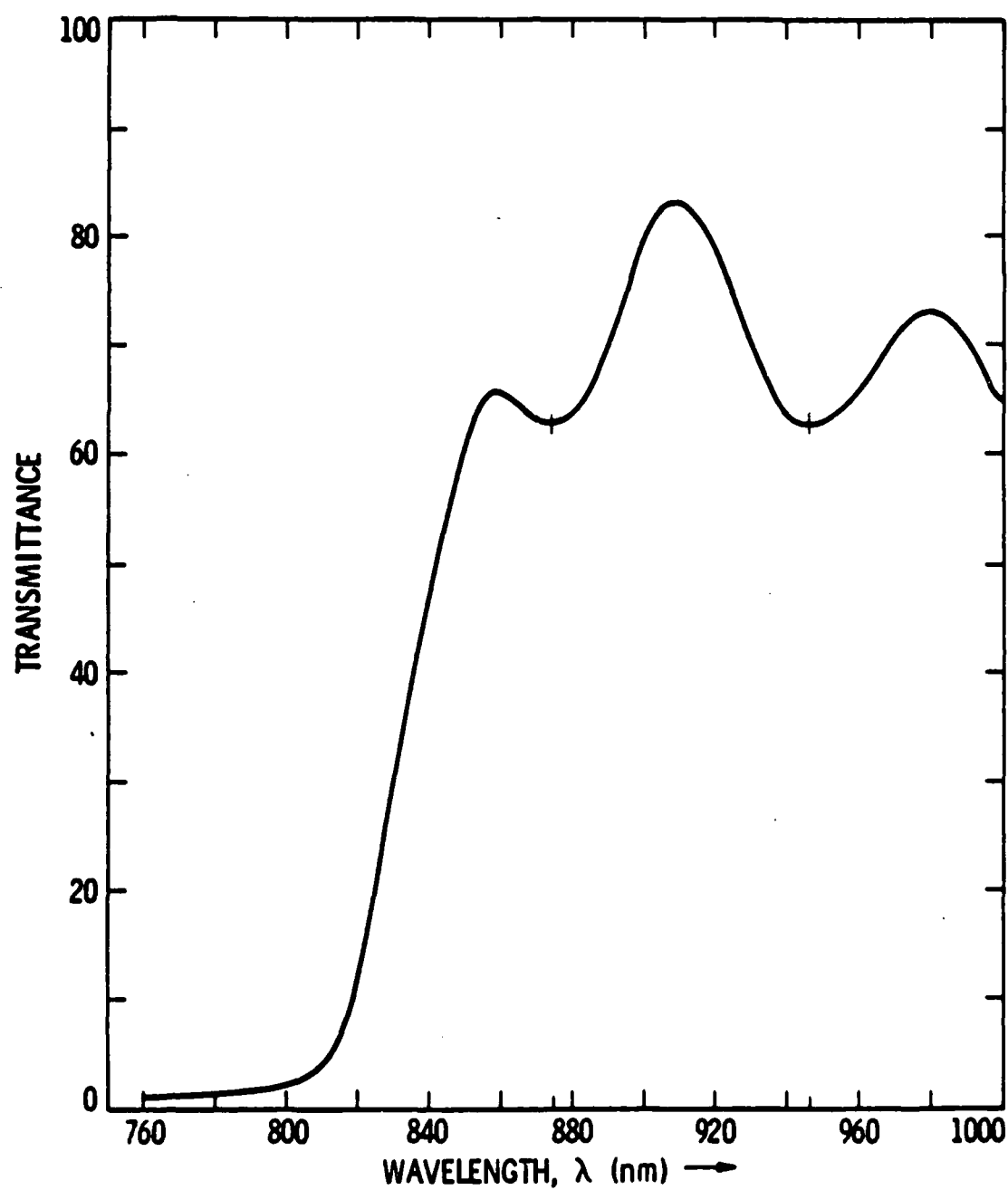
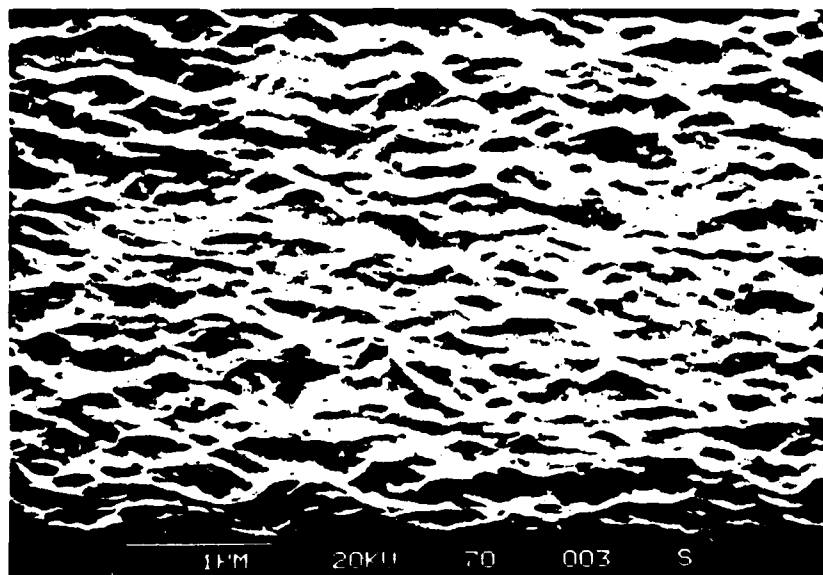Figure 3. Optical transmission spectrum of CdTe.

Figure 4. Scanning electron micrograph of CdTe film
deposited on glass by UV laser photolysis
showing excellent surface morphology. The
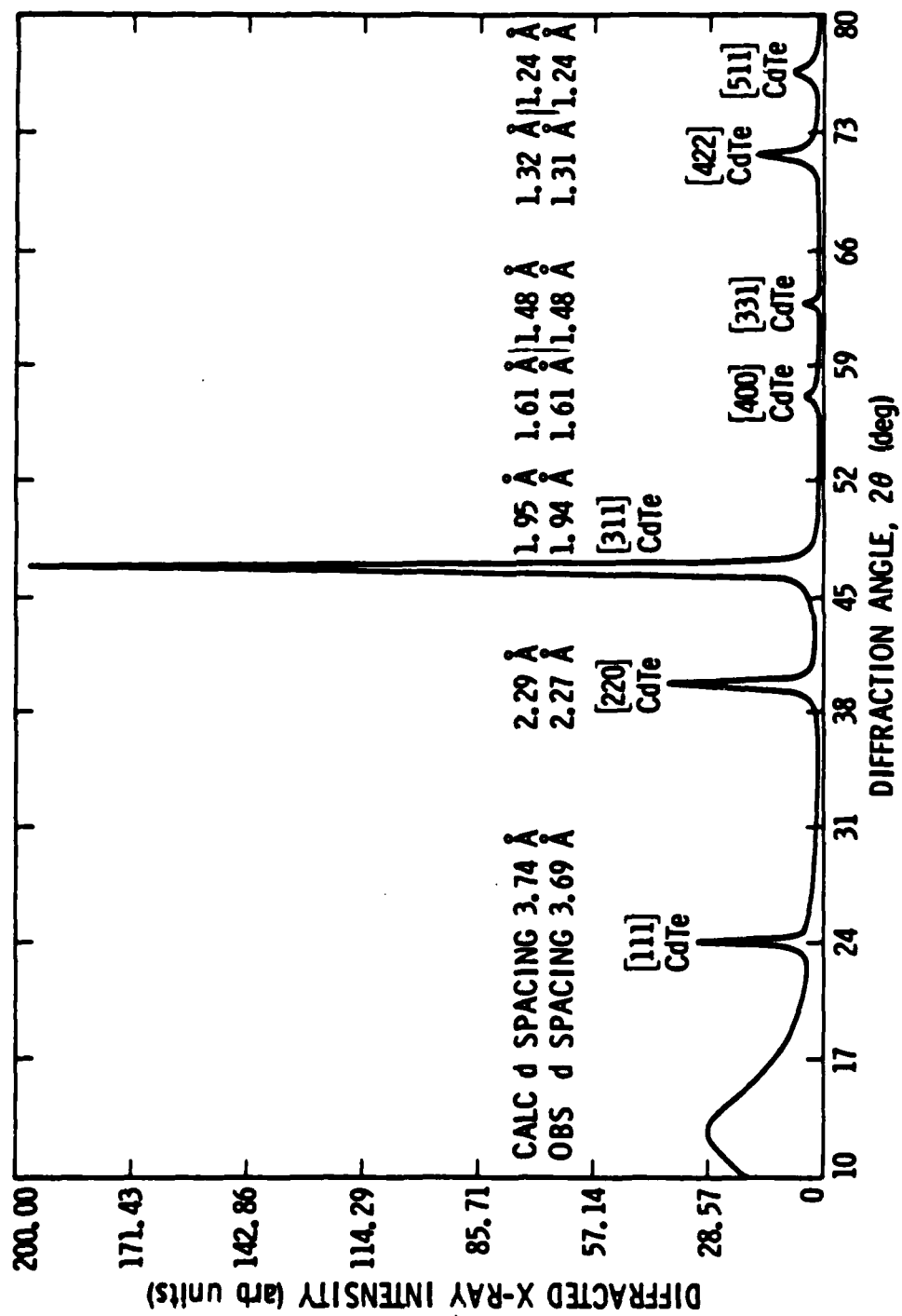marker length is 1 μm and the tilt angle
is 70°.

Figure 5. X-ray diffraction of a film of cadmium telluride deposited on a glass substrate using the laser photochemical technique.

planar and cross-sectional TEM and photoluminescence will be the primary means of characterizing the material, utilizing a collaboration with the University of Southern California.

The laser photochemical deposition studies will focus primarily on CdTe and ZnTe epitaxial growth on GaAs, studying in particular the role of source partial pressure, total pressure including the carrier gas H_2 or He, and photon flux density for both parallel and perpendicular geometries. Similar characterization as mentioned above will be utilized for growth optimization.

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APPENDIX A

HETEROEPITAXIAL GROWTH

OF $Cd_{1-x}Mn_xTe$ ON GaAs BY

METALORGANIC CHEMICAL VAPOR DEPOSITION

Heteroepitaxial growth of $Cd_{1-x}Mn_xTe$ on GaAs by metalorganic chemical vapor deposition

Akbar Nouhi and Richard J. Stirn

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

In this letter we report on preliminary results of heteroepitaxial growth of the dilute magnetic semiconductor alloy $Cd_{1-x}Mn_xTe$ on GaAs by metalorganic chemical vapor deposition. Dimethylcadmium (DMCd), diethyltellurium (DETe), and tricarbonyl (methylcyclopentadienyl) manganese (TCPMn) were used as source materials. The TCPMn had to be heated to as high as 140 °C to provide the required vapor pressure. Films with Mn atomic fractions up to 30% have been grown over the temperature range 410–450 °C. Results of optical absorption/transmission, photoluminescence, and x-ray diffraction measurements are presented along with a scanning electron micrograph showing good surface morphology of the grown layers.

The CdTe-MnTe alloy system is one class of materials referred to as dilute magnetic semiconductors (DMS's) and one that is most extensively studied. Single phase solid solutions with zinc-blende structure are formed in $Cd_{1-x}Mn_xTe$ with $0 < x < 0.7$. The energy gap at room temperature ($E_g = 1.50 + 1.34x$ eV) and lattice constant ($a_0 = 6.487 - 0.149x$ Å)[1] vary linearly throughout this range even though MnTe has a different structure (nickel arsenide) from that of CdTe (zinc blende). The presence of the paramagnetic manganese ions in the host lattice (CdTe) gives rise to interesting magnetic and magneto-optical properties because of spin-exchange interactions with conduction-band electrons and valence-band holes which modify the band structure. Such interesting phenomena include a giant Faraday rotation near the fundamental absorption edge,[2] an extremely large negative magnetoresistance,[3] Stokes-shifted spin-flip Raman scattering,[4] and very large electronic g factors.[5]

It is only during the last several years that heteroepitaxial thin films of (CdMn)Te have been deposited by molecular beam epitaxy (MBE) mostly on GaAs substrates,[6] and subsequently, multiple quantum well and superlattice structures.[7,8] These structures have exhibited strong photoluminescence (PL), stimulated emission,[9] and magnetically tunable lasing action.[10] To our knowledge, there has been no report of (CdMn)Te deposition by metalorganic chemical vapor deposition (MOCVD) techniques, although high-quality heteroepitaxial CdTe films have been grown on GaAs,[11-13] InSb,[12,14,15] and sapphire[16,17] substrates. The reason for this is probably the lack of a reasonably high vapor pressure metal alkyl source for Mn.

The growth system used consists of a horizontal quartz reactor tube operating at atmospheric pressure with a rf-heated graphite susceptor. The metalorganic sources for the Cd and Te were dimethylcadmium (DMCd) and diethyltellurium (DETe), respectively. The transport gas was palladium-diffused high-purity H_2. The DMCd source was held at a temperature of 0 °C and the DETe at 27 °C. The total flow rate of H_2 and metalorganics was about 4 ℓ/min corresponding to a linear flow velocity of about 3 cm/s over the substrate.

CdTe films were first grown at temperatures of 400–430 °C on GaAs substrates (100) misoriented 2° toward the (110) direction. The substrates were cleaned in organic solvents and etched by H_2SO_4:H_2O_2:H_2O (5:1:1) for 30 s. After loading the substrates, the system was pumped down to about 50 μTorr and then brought up to atmospheric pressure in H_2 at which time the substrate was heated to the growth temperature. The partial pressures of the Cd and Te sources during deposition were typically about 8×10^{-5} and 1.6×10^{-4} atm, respectively. CdTe films with 2 μm thicknesses were deposited with excellent surface morphology and crystallinity as reported by others elsewhere.[11-13]

For the growth of CdMnTe, the Mn source used was tricarbonyl(methycylopentadienyl) manganese (TCPMn) obtained from Alfa Products. TCPMn (M.P. = 1.5 °C) is a liquid at room temperature with vapor pressures of 0.5 and 12 Torr at 20 °C and 112 °C, respectively. No temperature dependence of the vapor pressure has been reported to our knowledge. Use of TCPMn as a source for Mn doping of MOCVD-grown ZnS and ZnSe epitaxial layers has been reported.[18] For constant deposition temperature and flow rates, the Mn concentration in the film increased exponentially with the temperature of the bubbler indicating a sharp increase in TCPMn vapor pressure as the source temperature is raised above about 100 °C. There was also an indication that the cracking temperature of TCPMn is about 450 °C with partial decomposition in the temperature range of 400–450 °C.

A number of depositions were made of CdMnTe on GaAs as well as on glass substrates using the same flow rates of H_2, DMCd, and DETe as used for CdTe deposition. The TCPMn source was heated to a temperature range of 120–140 °C in order to provide the required vapor pressure. The tubing, valves, and front end of the reactor tube were heated to about 100 °C to prevent condensation of the TCPMn that occurred in the absence of such heating. Substrate temperatures ranged from 410–450 °C.

Since the vapor pressure, and hence, mole fraction of the Mn source was not accurately known, a series of depositions was made on glass substrates and optical transmission measurements taken to determine the energy band gap. From these data the percentage of Mn in the deposited film was determined using the band-gap composition relation given
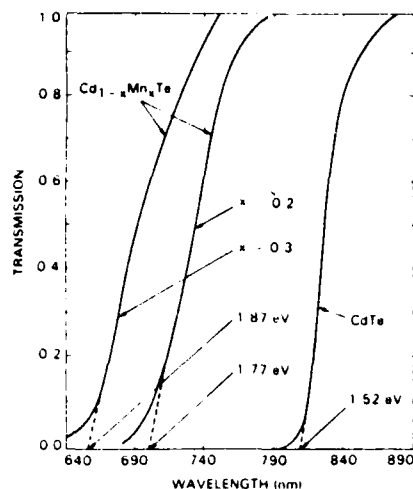
FIG. 1. Optical transmission curves for a CdTe film and two $Cd_{1-x}Mn_xTe$ films with $x = 0.1$ and 0.3.

FIG. 3. Photoluminescence at 10 K of a $Cd_{0.75}M_{0.25}Te$ film grown on a (100) GaAs substrate excited by the 488 nm line of an argon laser. The full width at half-maximum is 33 meV.

above.[1] Figure 1 shows the optical transmission curves for a CdTe film along with two $Cd_{1-x}Mn_xTe$ films with $x = 0.2$ and 0.3, with extrapolated band-gap energies (assuming constant reflection over the wavelength range) of about 1.52, 1.72, and 1.87 eV, respectively. These data match quite well with similar data for $Cd_{1-x}Mn_xTe$ films deposited by ionized cluster beams.[19]

As is the case for CdTe growth on GaAs, the orientation of the $Cd_{1-x}Mn_xTe$ crystalline layer on (100) GaAs was either (100) or (111) depending upon the initial growth conditions. This phenomenon has been observed for CdTe deposited by MBE[20] as well as for MOCVD,[21] and also reported for MBE-grown (CdMn)Te.[6] A model has been recently proposed for this dual mode of growth of CdTe on (100) GaAs,[22] which could possibly apply toward (CdMn)Te films with relatively low Mn concentration. Figure 2 shows two x-ray diffraction scans of the $Cd_{1-x}Mn_xTe$ film having slightly different thicknesses with $x = 0.2$. These data reproduce exactly those reported for MBE-grown $Cd_{1-x}Mn_xTe$ on GaAs.[6]

Strong photoluminescence was observed at low temperatures (10–15 K) in $Cd_{1-x}Mn_xTe$ films grown on (100) GaAs substrates, excited by the 488 nm line of an argon laser. Figure 3 shows the spectrum observed for a $Cd_{0.75}Mn_{0.25}Te$ film at $T = 10$ K. The full width at half-maximum (FWHM) of about 33 meV is an indication of
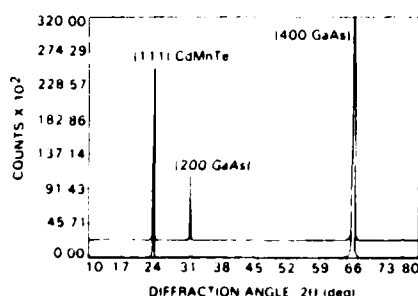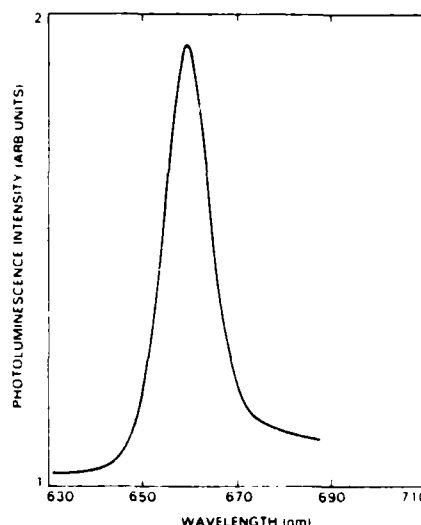
good crystalline quality of the layer. Low intensity broadband PL emissions originating from impurity and defect states were observed at longer wavelengths. Details of the study of these impurity/defect related emissions in relation to the growth conditions and Mn concentrations will be reported elsewhere.

The surface topography of CdTe films on GaAs was featureless when viewed with a light microscope showing no indication of cracking or peeling. The films also presented a "mirrorlike" reflectance to the naked eye with no cloudy areas. However, when Mn was added to the films, some cloudiness was observed. Attempts to improve the morphology with changes in the carrier gas flow rate, the mole fraction ratio of Te to Cd/Mn, and substrate temperature have been inconclusive to date. Nevertheless, we have occasionally obtained CdMnTe films having satisfactorily smooth and mirrorlike surface morphology (Fig. 4), indicating that the milky appearance of some films is probably related to pro-
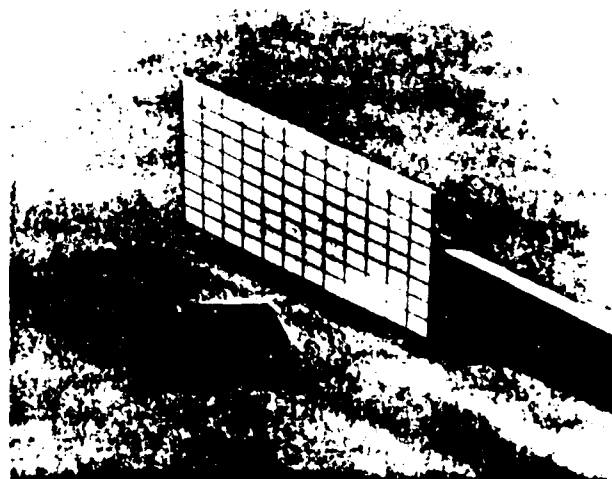

FIG. 2. X-ray diffraction curve for a 2-μm-thick $Cd_{0.8}Mn_{0.2}Te$ film on a (100) GaAs substrate.

FIG. 4. Photograph of a $Cd_{0.8}Mn_{0.2}Te$ layer on GaAs showing its specular characteristics.

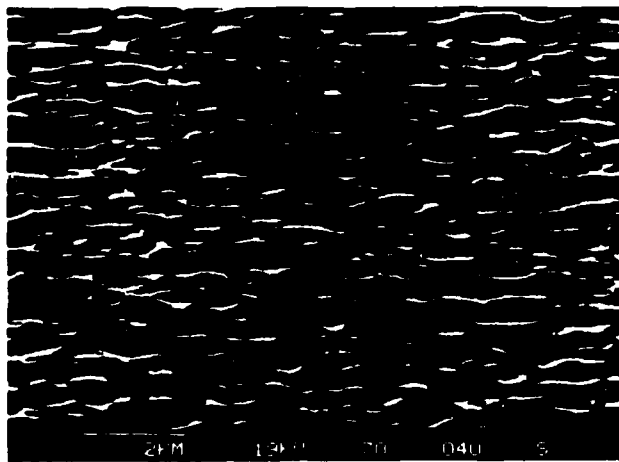2252   Appl. Phys. Lett., Vol. 51, No. 26, 28 December 1987

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FIG. 5. SEM micrograph of $Cd_{0.8}Mn_{0.2}Te$ layer on (100) GaAs misoriented $2° \rightarrow (110)$ showing surface morphology (tilt angle of 70°).

cess/system reproducibility rather than being an inherent material problem. For example, Ghandi et al. have reported the importance of remaining below 440 °C when growing CdTe on GaAs by MOCVD due to suspected Te crystallites forming on the substrate for films grown above that temperature.[13] A closer look at the surface by a scanning electron microscope (Fig. 5) shows a very light ripple effect with features having dimensions of about several thousand angstroms only.

In summary, we have demonstrated for the first time the feasibility of heteroepitaxial growth of $Cd_{1-x}Mn_xTe$ films on (100) GaAs substrates by atmospheric pressure MOCVD, with crystallographic properties similar to MBE-grown films. Films with Mn atomic fractions up to 30% have been grown with uniform Mn concentration throughout the film. Depositions of (CdMn)Te films with a band-gap energy of about 1.7 eV ($x = 0.10$) are now being done on CdS thin films for use as a higher band-gap solar cell on a cascaded multiple junction tandem solar cell. Results will be published elsewhere.

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APPENDIX B

HIGH RESOLUTION TRANSMISSION ELECTRON

MICROSCOPY INVESTIGATION OF THE

DEFECT STRUCTURE IN CdMnTe

Preprint

High Resolution Transmission Electron Microscopy
Investigation of the Defect Structure in CdMnTe Layers
Grown on GaAs by MOCVD

J. H. Mazur and P. Grodzinski
Materials Science Department
University of Southern California
Los Angeles, CA 90089-0241

A. Nouhi and R. J. Stirn
Jet Propulsion Laboratory
Pasadena, CA 91109

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF THE DEFECT STRUCTURE IN CdMnTe LAYERS GROWN ON GaAs BY MOCVD

J.H. MAZUR, P. GRODZINSKI, A. NOUHI* and R.J. STIRN*,
Materials Science Department, University of Southern California,
Los Angeles, CA 90089-0241
* Jet Propulsion Laboratory, Pasadena, CA 91109.

ABSTRACT

Electron diffraction and high resolution electron microscopy were used for analysis of $Cd_{1-x}Mn_xTe$ films grown on $(100)2^O[011]$ GaAs substrates by metal organic chemical vapor deposition (MOCVD) at 420^OC (x=0.3) and 450^OC (x=0.5). It has been found that these two conditions produce dramatically different microstructures. Two orientation relationships of the epilayers with respect to the substrate were observed. It is suggested that this phenomenon may be related to GaAs substrate surface morphology.

INTRODUCTION

The $Cd_{1-x}Mn_xTe$ alloy belongs to the class of diluted magnetic semiconductors (DMS). It crystallizes in the same zincblende structure (up to x = 0.71) as its host CdTe II-VI compound. Both the direct bandgap and lattice constant of $Cd_{1-x}Mn_xTe$ vary linearly with x fraction [1,2]. The band structure of $Cd_{1-x}Mn_xTe$, which is similar to that of CdTe [1,3], is changed dramatically in the presence of an external magnetic field. Another important property of $Cd_{1-x}Mn_xTe$ is a great Faraday rotation [1]. These properties of $Cd_{1-x}Mn_xTe$ were used in some prototype devices such as optical isolators [4]; also $Cd_{1-x}Mn_xTe$, due to a very good lattice match to HgCdTe, can be used as a buffer layer for (Hg,Cd)Te infrared detectors [5].

In this paper we report structural studies of $Cd_{1-x}Mn_xTe$ films grown on (100)GaAs by MOCVD. We investigated two specimens (x = 0.3 and x = 0.5) prepared at two different temperatures: 420^OC and 450^OC, respectively. This research, conducted with the use of transmission electron microscopy imaging and electron diffraction, was concentrated on determining the orientation relationships and structure of the $Cd_{1-x}Mn_xTe$/GaAs interface.

EXPERIMENTAL PROCEDURES

The CdMnTe epilayers were grown in a MOCVD system consisting of a horizontal quartz reactor operating at atmospheric pressure with an RF-heated graphite susceptor. The metal-organic sources used, were dimethylcadmium (DMCd), diethyltellurium (DETe) and tricarbonyl (methycyclopentadienyl) manganese (TCPMn). The carrier gas was palladium-diffused high-purity H_2. The TCPMn source was heated to a temperature range of $120-140^OC$ in order to provide the required vapor pressure. Films with Mn concentration up to 60% were deposited on $(100)2^O[011]$ GaAs substrates at growth temperatures ranging from 410 to 450^OC. However, this paper only reports TEM results for layers with a concentration of 50 and 30% Mn. The details of the growth procedures are described elsewhere [6]. The TEM observations of cross-sections along [011] were performed using Philips 420T, JEOL 200CX, and JEOL 4000EX electron microscopes operating at 120, 200, and 400 kV, respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

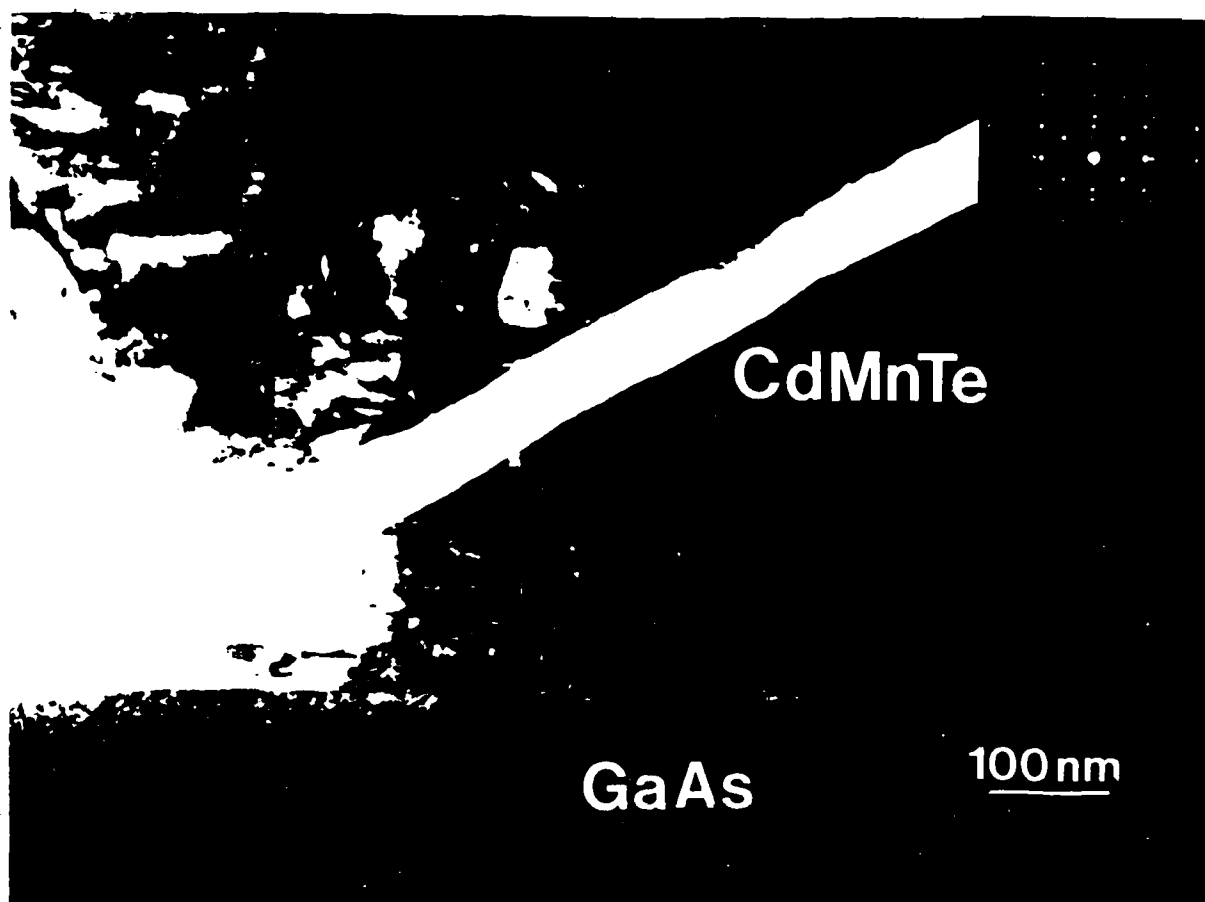Figure 1 shows a low magnification bright field multi-beam image

Fig. 1.
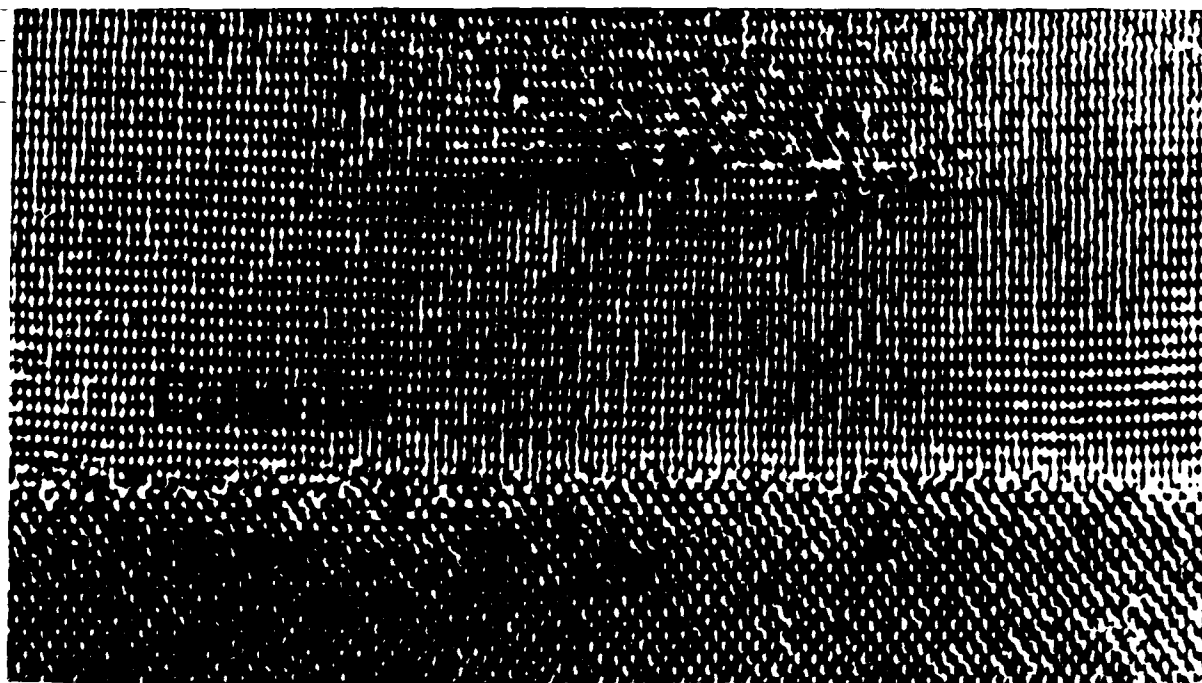Low magnification multi-beam bright-field image of the $Cd_{1-x}Mn_xTe$ (x = 0.3) layer grown at 420°C.

Fig. 2.
A high resolution image of the $Cd_{1-x}Mn_xTe/GaAs$ interface along $[\bar{1}12]$ zone axis of $Cd_{1-x}Mn_xTe$.

of $Cd_{1-x}Mn_xTe$ grown on a (100) GaAs substrate. Non-parallel epitaxy orientation relationship $(100)_{GaAs}//(1\bar{1}1)_{CdMnTe}$, $[011]_{GaAs}//[110]_{CdMnTe}$, $[011]_{GaAs}//[11\bar{2}]_{CdMnTe}$ between the film and the substrate was found from the electron diffraction pattern included as an inset in Fig. 1.

Figure 2 shows HREM image of the GaAs/$Cd_{1-x}Mn_xTe$ interface illustrating such an orientation relationship. The interface is very abrupt with no intermediate phase present at the interface. The contrast along the interface changes, suggesting possible local deviations from the atomistic models proposed in the literature [7]. The $Cd_{1-x}Mn_xTe$ layer contains a considerable number of stacking faults and twins with the (111) fault or twin planes parallel to the GaAs/$Cd_{1-x}Mn_xTe$ interface. Additional defects are observed in the images at the termination of stacking faults and at incoherent twin boundaries. These defects could be caused by sets of partial dislocations and products of their interactions.

Figure 3 shows low magnification multi-beam bright-field image of $Cd_{1-x}Mn_xTe$ (x=0.5) grown at 450°C. The film is polycrystalline with the grains 10-1,000 nm in size. A selected area diffraction pattern (SAD) included as an inset, indicated the presence of grains having two types of epitaxial orientation relationships with the substrate: (i) $(100)_{GaAs}$ // $(1\bar{1}1)_{CdMnTe}$, $[011]_{GaAs}$ // $[110]_{CdMnTe}$, $[011]_{GaAs}$ // $[11\bar{2}]_{CdMnTe}$ (non-parallel epitaxy), and (ii) $(100)_{GaAs}$ // $(100)_{CdMnTe}$, $[011]_{GaAs}$ // $[011]_{CdMnTe}$, $[01\bar{1}]_{GaAs}$ // $[01\bar{1}]_{CdMnTe}$ (parallel epitaxy). Parallel epitaxy appears to be associated with the presence of V-shaped groves; however it has also been found in regions with the shallower hemispherical pits (Fig. 4). The mismatch in this case is accommodated by closely spaced misfit dislocations, mostly of edge character. Non-parallel epitaxy appears to be associated with planar or stepped GaAs surface regions. These observations are similar to those, done in the case of CdTe layers grown on GaAs by MBE [8]. It is interesting to note, that the non-parallel epitaxy is energetically more a favorable configuration, as it reduces the misfit along $[011]_{GaAs}$ // $[11\bar{2}]_{CdMnTe}$ to less than 0.7%, while retaining larger than 12% misfit (typical for parallel epitaxy) along $[01\bar{1}]_{GaAs}$ // $[110]_{CdMnTe}$. However, other factors such as substrate surface preparation and growth kinetics might be also important in determination of overlayer orientation. Work in progress is attempting to determine factors relevant for control of the epitaxy type.
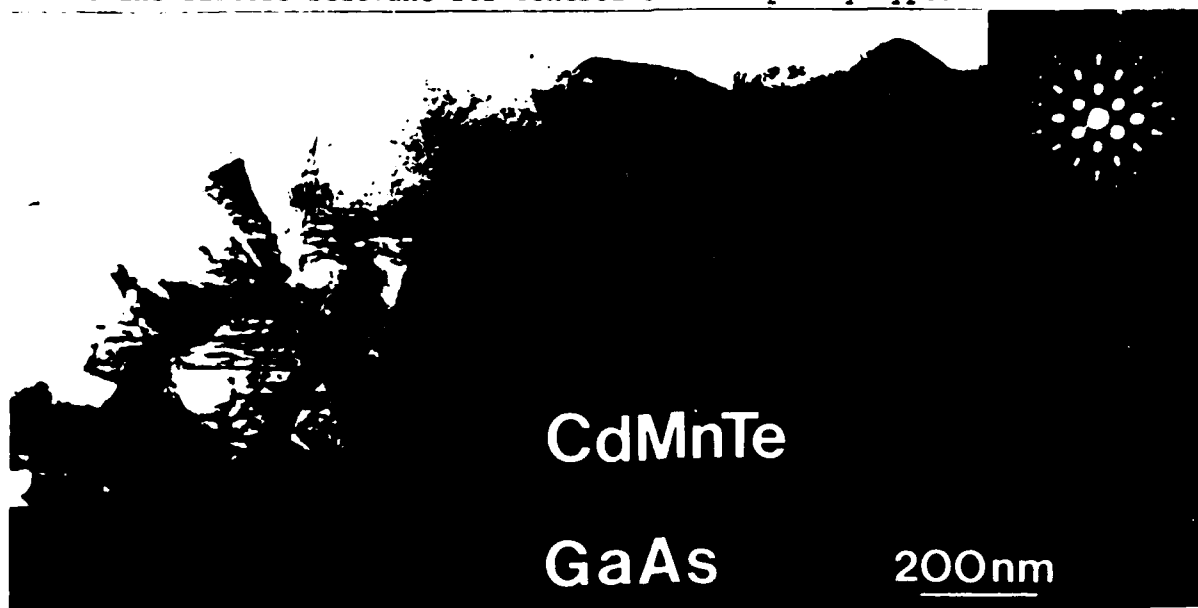

Fig. 3
Low magnification multi-beam bright-field image of $Cd_{1-x}Mn_xTe$ (x = 0.5) grown at 450°C by MOCVD.

Fig. 4.
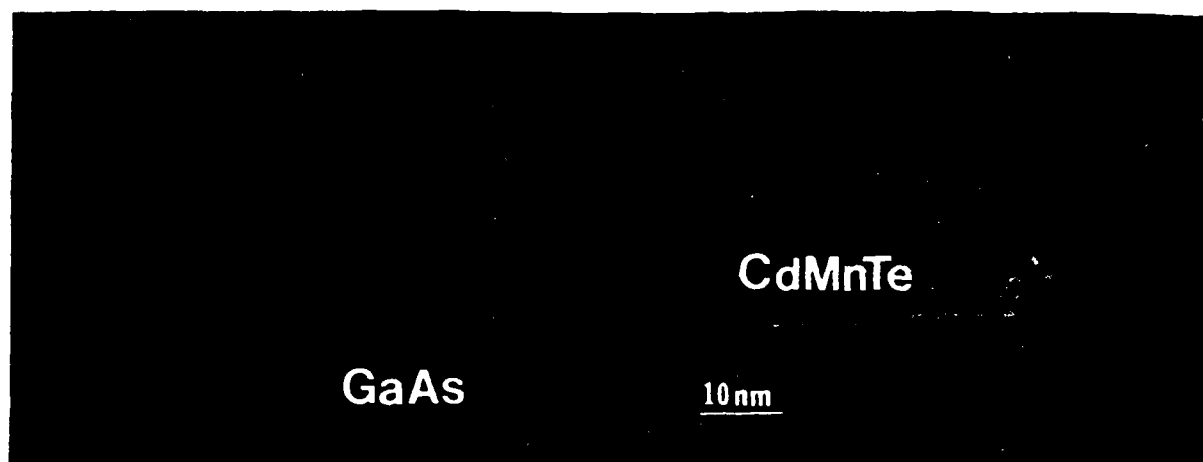A high resolution image of the $Cd_{1-x}Mn_xTe$/GaAs interface showing two grains exhibiting two different types of epitaxy.

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